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6. AUTHORS

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14. ABSTRACT

This project seeks to investigate and quantify inter-relationships between the compositional, morphological, and functional properties of nanofiber composite anion-exchange membranes for alkaline fuel cells. A new membrane fabrication strategy, utilizing polymer fiber electrospinning, will be employed to make hydroxide-conducting membranes with an entirely new morphology, where one electrospun polymer provides pathways for ion conductivity and the second electrospun polymer restricts ionomer swelling and imparts mechanical strength to the membrane. The functional ionomer/polyelectrolyte and the inert support polymer are electrospun simultaneously

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Peter Pintauro
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Report Title

Final Report: Nanofiber Composite Membranes for Alkaline Fuel Cells: Generation of Compositional, Morphological, and Functional Property Relationships (Electrochemistry and Advanced Energy Conversion)

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This project seeks to investigate and quantify inter-relationships between the compositional, morphological, and functional properties of nanofiber composite anion-exchange membranes for alkaline fuel cells. A new membrane fabrication strategy, utilizing polymer fiber electrospinning, will be employed to make hydroxide-conducting membranes with an entirely new morphology, where one electrospun polymer provides pathways for ion conductivity and the second electrospun polymer restricts ionomer swelling and imparts mechanical strength to the membrane. The functional ionomer/polyelectrolyte and the inert support polymer are electrospun simultaneously using separate spinnerets. Post-treatment will convert the dual-fiber mats into defect-free membranes, while maintaining the nanofiber morphology of the ionomer/polyelectrolyte component. Membranes will be made where ion-exchange polymer nanofibers are surrounded by an inert (uncharged) polymer matrix. The dual fiber electrospinning technique circumvents the need for a separate polymer impregnation step, which simplifies membrane fabrication and minimizes defect pinhole formation. Methods for fabricating such membranes are to be identified and the transport, swelling, and mechanical properties of the final membranes are to be measured and contrasted with the properties of homogeneous ionomer films. A series of model membranes will be fabricated with a range of well defined and carefully measured compositions and nanofiber morphologies. From these membranes, fundamental structure/function relationships will be generated.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
08/10/2015	5.00	Andrew Park, Forbes Turley, Ryszard Wycisk, Peter Pintauro. Diol-Crosslinked Electrospun Composite Anion ExchangeMembranes , Journal of the Electrochemical Society, (06 2015): 560. doi:
12/04/2015	7.00	Forbes Turley, Peter Pintauro, Andrew Park,, Ryszard Wycisk, Xiaoming Ren. Crosslinked poly (phenylene oxide)-based nanofiber composite membranes for alkaline fuel cells, Chemistry of Materials A, (01 2016): 0. doi:
TOTAL:		**2**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
11/24/2014	4.00	Forbes E. Turley, Andrew M. Park, Ryszard J. Wycisk, Peter N. Pintauro. Electrospun and Cross-Linked Nanofiber Composite Anion Exchange Membranes, Macromolecules, (01 2014): 227. doi:
12/09/2015	8.00	A. M. Park, P. N. Pintauro. Electrospun Composite Membranes for Alkaline Fuel Cells , ECS Transactions, (01 2011): 1817. doi:
TOTAL:		**2**

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Oral Presentations:

Nanofiber Composite Membranes for Alkaline Fuel Cells, Andrew M. Park and Peter N. Pintauro, Fall Electrochemical Society Meeting, 2011, Boston, MA

Nanofiber Composite Ion-Exchange Membranes, Jason Ballengee, Andrew Park, and Peter N. Pintauro, International Congress on Membranes, July 2011, Amsterdam, Netherlands

Nanofiber Electrospinning for Anion-Exchange Membrane and Fuel Cell Electrode Fabrication, P. N. Pintauro, Army Research Laboratory, July 2012 (Invited Talk)

Nanofiber Composite Ion-Exchange Membranes, P. N. Pintauro, University of Padua, Padua, Italy, September 2012 (Invited Talk)

Proton and Hydroxide Ion Conducting Nanofiber Composite Fuel Cell Membranes
Peter N. Pintauro, Jason B. Ballengee, Andrew M. Park, and Ryszard Wycisk
Asilomar Conference on Proton Conducting Fuel Cell Membranes, Pacific Grove, CA February 2013. (Invited Talk)

Electrospun Nanofiber Membranes and Electrodes for Energy Applications, Jason Ballengee, Andrew Park, Ryszard Wycisk, Ethan Self, and Peter Pintauro American Chemical Society Conference, Indianapolis, IN, September 2013. (Invited Talk)

Fabrication and Properties of Electrospun Fuel Cell Membranes, Jason B. Ballengee, Andrew Park, Jun Woo Park, Ryszard Wycisk and Peter N. Pintauro, Spring Electrochemical Society Meeting, 2013, Toronto, Canada

Novel Electrospun and Crosslinked Nanofiber Composite Anion-Exchange Membranes, Andrew M. Park, Forbes E. Turley, Ryszard Wycisk, and Peter N. Pintauro, Fall Electrochemical Society Meeting, 2013, San Francisco, CA

Evaluation of Cation and Backbone Chemistries for Electrospun and Crosslinked Nanofiber Composite Anion Exchange Membranes, Andrew M. Park, Forbes E. Turley, Ryszard J. Wycisk, and Peter N. Pintauro, Fall Electrochemical Society Meeting, 2014, Cancun, Mexico.

Electrospun Nanofiber Anion-Exchange Membranes for Alkaline Fuel Cells, Peter N. Pintauro, Department of Chemistry, University of Montpellier, Montpellier, France, June 2014 (Invited Seminar).

Hydroxide Ion Conducting Fuel Cell Membranes Based on Polymer Nanofiber Electrospinning, Andrew M. Park, Peter N. Pintauro, and Ryszard Wycisk, Advances in Polymers for Fuel Cells and Energy Devices, February 8-11, 2015, Asilomar Conference Grounds, Pacific Grove, California (Invited Talk).

Posters:

Andrew Park, Ryszard Wycisk and Peter Pintauro, Electrospun and Crosslinked Nanofiber Composite Anion Exchange Membranes, Gordon Research Conference on Fuel Cells, Bryant University, Smithfield, RI, August 2014

Number of Presentations: 12.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper	
08/29/2013	1.00	A.M. Park, F.E. Turley, R.J. Wycisk, and P.N. Pintauro. Polysulfone-Based Electrospun and Crosslinked Anion Exchange Membranes, Electrochemical Society Transactions. 26-OCT-13, . : ,

TOTAL: **1**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper	
08/10/2015	6.00	Andrew Park, Ryszard Wycisk, Xiaoming Ren, Forbes Turley, Peter Pintauro. Crosslinked Poly(phenylene oxide)-Based Nanofiber Composite Membranes for Alkaline Fuel Cells , Chemistry of Materials A (08 2015)
10/15/2014	3.00	A. M. Park, F. E. Turley, R. Wycisk, P. N. Pintauro. Polysulfone-Based Electrospun Anion Exchange Membranes, ECS Transactions (10 2013)
10/15/2014	2.00	Forbes E. Turley, Andrew M. Park, Ryszard J. Wycisk, Peter N. Pintauro. Electrospun and Cross-Linked Nanofiber Composite Anion Exchange Membranes, Macromolecules (01 2014)

TOTAL: **3**

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Composite Membranes, Methods of Making Same and Applications of Same

Patents Awarded

Awards

Fellow, the American Institute of Chemical Engineers (2014)
Fellow, the Electrochemical Society (2010)

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Andrew M. Park	0.77	
FTE Equivalent:	**0.77**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Peter N. Pintauro	0.11	
FTE Equivalent:	**0.11**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Forbes Turley	0.13	Biomedical Engineering
Tori Trout	0.20	
FTE Equivalent:	**0.33**	
Total Number:	**2**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	2.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:	2.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:	1.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME	
Andrew M. Park	
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED
Ryszard Wycisk	0.17
FTE Equivalent:	**0.17**
Total Number:	**1**

Sub Contractors (DD882)

Inventions (DD882)

5 **Composite Membranes, Methods of Making Same, and Applications of Same**

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) Y

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2): Germany, France, Japan, Korea, China, U.K.

5a: Peter Pintauro

5f-1a: Vanderbilt University

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Brentwood TN 37027

5a: Ryszard Wycisk

5f-1a: Vanderbilt University

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5a: Jason Ballengee

5f-1a: Vanderbilt University

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Nashville TN 37235

5a: Andrew Park

5f-1a: Vanderbilt University

5f-c: 2400 Highland Avenue

Nashville TN 37235

Scientific Progress

See Attachment

Technology Transfer

Nanofiber Composite Ion Exchange Membrane technology was licensed to Merck, KGaA (2015)

Final Report to the Army Research Office

for

Nanofiber Composite Membranes for Alkaline Fuel Cells: Generation of Compositional, Morphological, and Functional Property Relationships

Agreement Number: W911NF-11-1-0454

Principal Investigator: Peter Pintauro

December 1, 2015

1. Introduction

1.1 Statement of the Problem Studied

This project seeks to investigate and quantify inter-relationships between the compositional, morphological, and functional properties of nanofiber composite anion-exchange membranes for alkaline fuel cells. A new membrane fabrication strategy, utilizing polymer fiber electrospinning, will be employed to make hydroxide-conducting membranes with an entirely new morphology, where one electrospun polymer provides pathways for ion conductivity and the second electrospun polymer restricts ionomer swelling and imparts mechanical strength to the membrane. The functional ionomer/polyelectrolyte and the inert support polymer are electrospun simultaneously using separate spinnerets. Post-treatment will convert the dual-fiber mats into defect-free membranes, while maintaining the nanofiber morphology of the ionomer/polyelectrolyte component. Membranes will be made where ion-exchange polymer nanofibers are surrounded by an inert (uncharged) polymer matrix. The dual fiber electrospinning technique circumvents the need for a separate polymer impregnation step, which simplifies membrane fabrication and minimizes defect pinhole formation. Methods for fabricating such membranes are to be identified and the transport, swelling, and mechanical properties of the final membranes are to be measured and contrasted with the properties of homogeneous ionomer films. A series of model membranes will be fabricated with a range of well defined and carefully measured compositions and nanofiber morphologies. From these membranes, fundamental structure/function relationships will be generated.

1.2 Background

An AEM must have the following properties: (1) zero electronic conductivity, (2) high hydroxide ion conductivity, (3) robust mechanical properties, (4) excellent chemical stability, and (5) low cost. One of the biggest challenges is the seeming dichotomy between membrane conductivity and mechanical properties. The most common approach to raise membrane conductivity is to increase the ion exchange capacity (IEC) of the ionomer by tethering more cationic groups to the polymer backbone. As the concentration of these charges increases, however, the mechanical

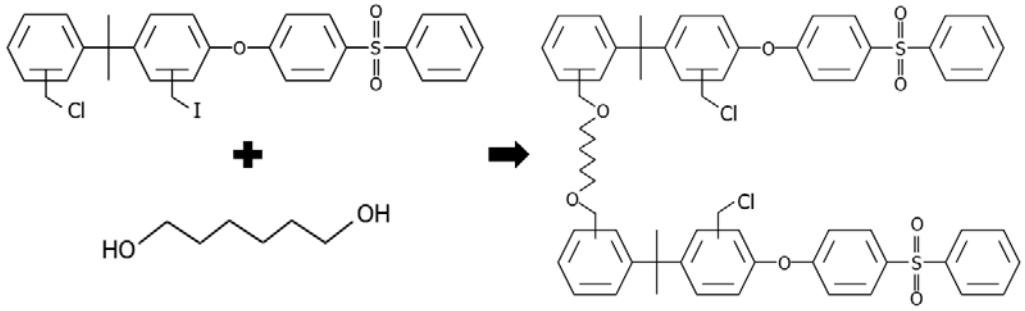
properties of the membrane worsen, in terms of brittleness in the dry state and/or unacceptably high water uptake (swelling) and a loss of mechanical integrity when fully hydrated. Some polymers can achieve such a high IEC as to become soluble in water, a critical problem in a water-rich fuel cell environment. Many researchers have recently tried to address this problem by fabricating membranes of a homogeneous anion-exchange polymer. These investigations have generated high interest in AEM materials, but there is significant room for improving both the membrane conductivity and mechanical properties.

Park and Pintauro have used this dual-fiber electrospinning technique in Year 1 to produce a mechanically stable anion exchange membrane with good conductivity. Instead of directly spinning the ionomer, an uncharged chloromethylated precursor, chloromethyl polysulfone (CMPSF), was electrospun concurrently with the uncharged/inert reinforcing polymer polyphenylsulfone (PPSU). The fibers of CMPSF were subsequently treated with trimethylamine, which converted the chloromethyl groups on the polymer backbone into quaternary ammonium moieties, forming quaternary ammonium polysulfone (QAPSF) fibers. The mat of QAPSF and PPSU fibers was then processed into a dense membrane where the QAPSF fibers were surrounded by an inert matrix of PPSU. These membranes exhibited improved mechanical and conductive properties when compared to a homogeneous film of QAPSF, including a conductivity of 0.04 S/cm at room temperature in liquid water, a 93% gravimetric water swelling, and a 23 MPa stress-at-break. While the conductivity was good when compared to other anion exchange membranes in the literature, it still is much lower than that of Nafion. To compete with PEMFCs for high power applications, the conductivity of the AEM must be improved while maintaining mechanical integrity. Theoretically, the maximum IEC for a neat QAPSF membrane is 3.4 mmol/g, but QAPSF is water soluble at an IEC greater than ~2.5 mmol/g. It would be desirable to create a membrane with a very high IEC (>2.5 mmol/g) polymer without water dissolution.

The strategy employed during Year 2 of this ARO project was to utilize high IEC crosslinked quaternary polysulfone polymers in nanofiber composite membranes, where diol crosslinking was used to prevent ionomer dissolution in water. A precise stoichiometric amount of an aliphatic diol molecule (e.g., 1,6-hexanediol) was added to a polysulfone polymer with chloromethylated and some iodomethylated groups. When subjected to heating, the diol reacted with the iodomethyl groups to form di-ether linkages between polymer chains. The crosslinking reaction scheme is shown in Scheme 1. The result is a tunable crosslinking scheme that preserves most of the chloromethyl groups for eventual conversion to quaternary ammonium anion-exchange sites. The conductivity, water swelling, and mechanical properties of the resulting nanofiber composite membranes was determined (see 2012 annual report).

In Year 3, a second polymer crosslinking procedure has been employed to make AEMs with a diamine crosslinker, where the ionomer fiber IEC is very high and where the uncharged polymer controls fiber swelling and imparts good mechanical properties to the membrane. The work builds upon the prior successes of the project PI, who developed a dual fiber electrospinning approach for preparing nanofiber composite proton-exchange membranes. The present work is also a direct extension of the PI's diol crosslinking work from Year 2 of this ARO project and from a dual fiber AEM study that was published by Park and Pintauro, where

uncrosslinked polysulfone fibers with a moderate concentration of tetramethylammonium fixed charge sites were embedded in a poly(phenylsulfone) (PPSU) matrix.



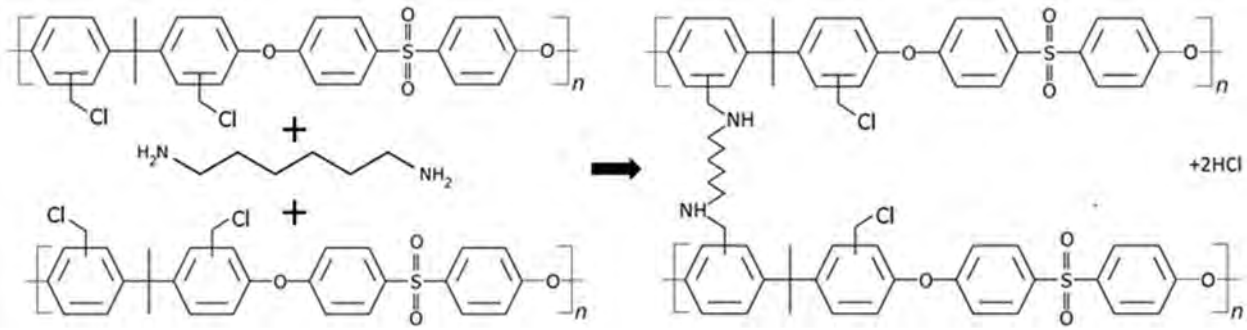
Scheme 1. Crosslinking scheme for chloromethylated and iodomethylated polysulfone with a diol crosslinker.

To make highly conductive fiber composite AEMs, a mat containing chloromethylated polysulfone fibers (where the degree of chloromethylation was > 95%) and PPSU fibers was immersed in an aliphatic diamine crosslinker (the polymer crosslinking reaction is shown in Scheme 2). The mat was then exposed to chloroform vapors which selectively softened the PPSU and allowed it to flow and fill the void space between the crosslinked chloromethyl-containing fibers. Finally, the chloromethyl groups were converted to tetramethylammonium ion exchange sites by reaction with trimethylamine. The crosslinking step was necessary because the IEC of the quaternized polysulfone fibers was far greater than their water solubility limit.

The focus of the present study was on changing the degree of crosslinking of the ionomer fibers, where all membranes were made from the same chloromethylated polysulfone (a degree of chloromethylation of 1.94, which would produce an ionomer IEC of 3.32 mmol/g after complete quaternization). Membranes were also made with different ratios of chloromethylated ionomer precursor to polyphenylsulfone to examine the effect of uncharged polymer content on membrane properties. Composite membranes were tested for ion exchange capacity, OH^- conductivity after equilibration in room temperature liquid water, equilibrium gravimetric water swelling, methanol permeability, mechanical properties, and chemical stability.

Also in Year 3, membranes were prepared by simultaneously electrospinning brominated poly(phenylene oxide) (PPO) and polyphenylsulfone (PPSU) to form a dual fiber mat. The mat was then soaked in a hexamethylenediamine solution to create a small number of crosslinks in the PPO fibers (preventing water solubility when charged groups were added to the PPO), as shown in Scheme 3. Subsequent mat processing included mechanical compaction, exposure to chloroform vapor (which softened the polyphenylsulfone, allowing it to flow and fill the void space between crosslinked brominated PPO fibers), and reaction of the resulting films with either trimethylamine or 1,2-dimethylimidazole to create cationic groups at those bromomethyl sites of PPO which did not react with diamine crosslinker. The final composite membranes were tested for hydroxide ion conductivity, gravimetric water uptake, mechanical properties in the wet and dry states, and chemical stability in hot KOH. The most conductive membrane was converted

into a fuel cell membrane-electrode-assembly and tested in an alkaline fuel cell at 60°C with H_2 and O_2 feed gases.



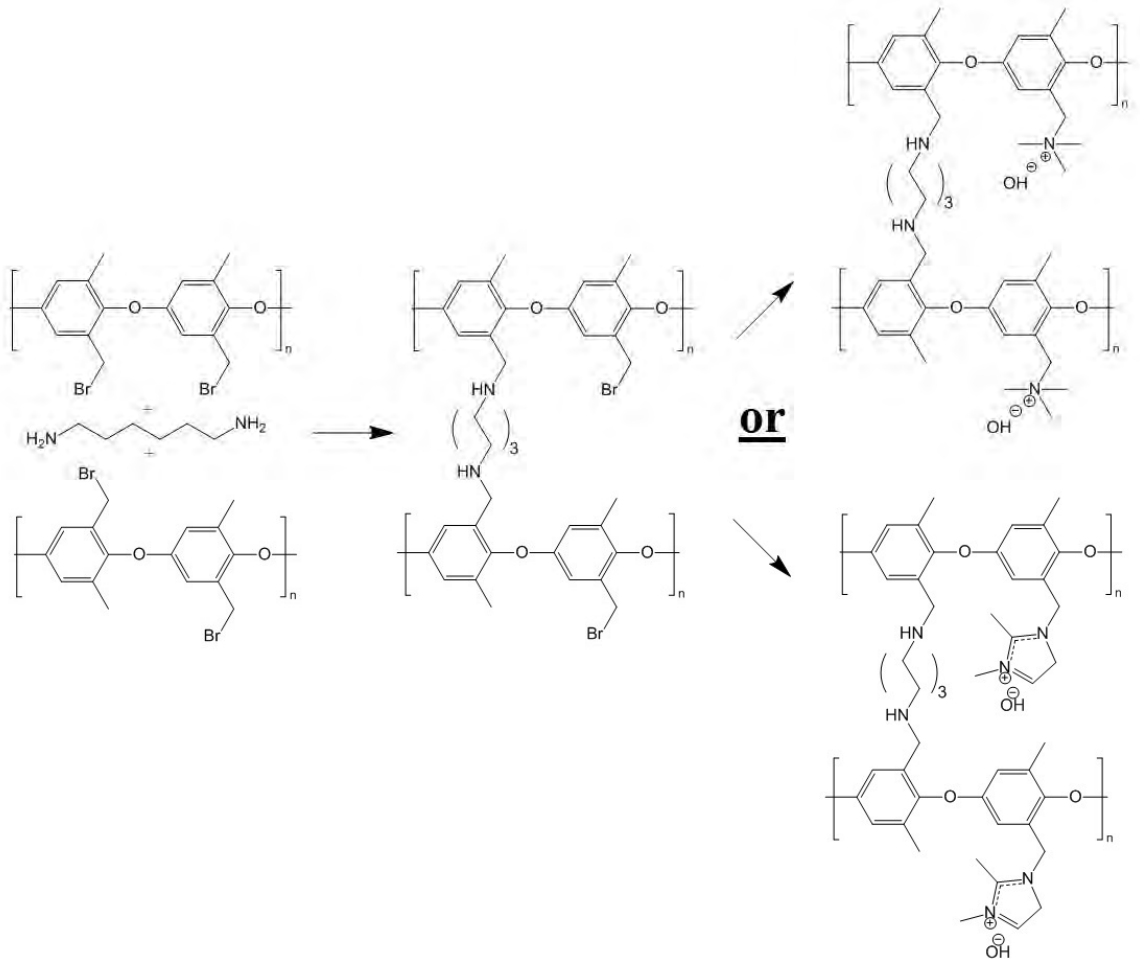
Scheme 2. Scheme for reacting chloromethylated polysulfone (CMPSF) with diamine (pictured: hexamethylenediamine) to create crosslinked polysulfone

The degree of crosslinking and the ratio of uncharged PPSU to functionalized poly(phenylene oxide) polyelectrolyte were varied to yield composite membranes with an effective ion exchange capacity (IEC) ranging from 1.2-2.8 mmol/g. A membrane with benzyl trimethylammonium-functionalized polyelectrolyte fibers (4.0 mmol/g IEC) with 15% crosslinks and 50 wt.% uncharged PPSU exhibited a high hydroxide ion conductivity in water at 23°C (66 mS/cm), reasonable water swelling (96%), robust mechanical properties (15 MPa stress-at-break in the hydrated state), and good chemical stability in 1.0 M KOH at 60°C. Initial hydrogen/oxygen fuel cell tests with this membrane (40 μm thick) were promising, with a peak power density of 320 mW/cm^2.

2. Summary of the Most Important Results

2.1 Diol-Crosslinked AEMs

Nanofiber composite alkaline fuel cell anion exchange membranes were fabricated and characterized, where an interconnected network of submicron diameter fibers of anion exchange polymer (crosslinked polysulfone with either benzyl trimethylammonium, 1-methylimidazolium, or 1,2-dimethylimidazolium fixed charge groups) was embedded in a polyphenylsulfone matrix. A dual fiber membrane fabrication procedure was employed, where chloromethylated/iodomethylated polysulfone nanofibers containing 4.0-10.0 mol% 1,6-hexanediol crosslinker were electrospun simultaneously with polyphenylsulfone fibers. The resultant dual fiber mat was subsequently processed into a dense and defect-free anion exchange membrane by heating to create diol crosslinks, exposure to chloroform vapor which softened the polyphenylsulfone and allowed it to fill the space between crosslinked fibers, and functionalization of the chloromethyl/iodomethyl fibers with trimethylamine, 1-methylimidazole, or 1,2-dimethylimidazole. All membranes contained 65 wt.% polyelectrolyte fibers and 35 wt.% polyphenylsulfone, where the ion exchange capacity of the crosslinked fibers was 2.5-3.0



Scheme 3. Scheme for reacting brominated poly(phenylene oxide) with hexamethylenediamine crosslinker and conversion of the remaining bromide sites to benzyl trimethylammonium or 1,2-dimethylimidazolium form.

mmol/g, well above the water solubility limit for uncrosslinked polysulfone with benzyl trimethylammonium or imidazolium fixed-charged groups. The in-plane OH^- ion conductivity of the resulting nanofiber composite membranes was high (up to 57 mS/cm in water at room temperature at 8% crosslinking degree). The presence of polyphenylsulfone matrix material reduced water swelling and improved membrane mechanical properties. As an example of overall membrane properties, a diol-crosslinked nanofiber composite film with 1,2-dimethylimidazolium charged sites exhibited a high OH^- conductivity in room temperature water (49 mS/cm), reasonable swelling (96%), good mechanical properties (16 MPa stress-at-break for a water equilibrated film), and reasonably good chemical stability.

2.2 Diamine-Crosslinked AEMs

A unique crosslinked nanofiber composite morphology was employed to create highly conductive and mechanically robust anion exchange membranes (AEMs) for alkaline fuel cells and electrodialysis separations. Chloromethylated polysulfone (CMPSF), the precursor for a

tetramethylammonium ionomer, and an inert reinforcing polymer, poly(phenylsulfone) (PPSU), were simultaneously electrospun from separate spinnerets into dual fiber mats. The mats were processed into dense and defect-free nanofiber composite anion exchange membranes by crosslinking a portion of the chloromethyl groups in the CMPSF fibers with an aliphatic diamine, softening the PPSU so that it flowed and filled the void space around the CMPSF fibers, and quaternizing the remaining chloromethyl groups of CMPSF. The final network of ionomer fibers embedded in a PPSU matrix had a very high ion exchange capacity (3.1 mmol/g) but was insoluble in water due to the presence of crosslinks. Membranes after processing were mechanically strong (in both the wet and dry states) with a very high hydroxide ion conductivity and moderate water swelling. Thus, a membrane containing 65 wt.% ionomer fibers had a OH^- conductivity of 65 mS/cm in water at 23^{o}C, a stress at break of 14 MPa (for a water-equilibrated membrane at room temperature), and an equilibrium liquid water swelling of 144% at 23^{o}C. The AEM fabrication scheme is robust and can easily be extended to different base polymers, ion exchange groups, and crosslinking schemes.

2.3 PPO-Based AEMS

High performance nanofiber composite anion exchange membranes were made where an interconnected fiber network of diamine-crosslinked poly(phenylene oxide)-based polyelectrolyte with either benzyl trimethylammonium or 1,2-dimethylimidazolium fixed charge groups was embedded in an uncharged matrix of reinforcing polyphenylsulfone (PPSU) polymer. Membranes were prepared by: (1) electrospinning brominated poly(phenylene oxide) (BrPPO) and PPSU simultaneously to create a dual fiber mat, (2) soaking the mat in a hexamethylenediamine solution to create inter-chain crosslinks at a limited number of bromomethyl sites in the BrPPO fibers, (3) exposing the mat to chloroform, which caused PPSU to flow and fill void space around the crosslinked BrPPO fibers, and (4) soaking the mat in a solution of either trimethylamine or 1,2-dimethylimidazole solution to convert remaining bromomethyl sites to fixed charge cationic moieties. A series of membranes were fabricated with an effective membrane ion exchange capacity (IEC) of between 1.2 and 2.8 mmol/g, where IEC was varied due to differences in: (1) the molecular weight of the fixed charge group, (2) the degree of fiber crosslinking, and (3) different amounts of PPSU in the final membrane (either 35 wt.% or 50 wt.%). For a membrane with 50 wt.% PPSU and benzyl trimethylammonium fixed charges with an effective membrane IEC of 2.0 mmol/g, the hydroxide ion conductivity in liquid water was high at 66 mS/cm, with reasonable water swelling (97% at room temperature). This membrane was mechanically strong, with a stress-at-break of 15 MPa when equilibrated in water at 23°C, and exhibited good chemical stability in a hot KOH solution. Preliminary experiments showed that nanofiber composite membranes were amenable to MEA fabrication, and such MEAs performed well in H_2/O_2 alkaline fuel cell tests, with a peak power of 320 mW/cm^2 at 60°C.

3. Conclusions

1. Four different types of nanofiber composite anion exchange membranes (AEMs) for potential use in an alkaline fuel cell were fabricated. The four membrane types are listed as follows:

   Type A - Polyelectrolyte nanofibers of polysulfone with benzyl trimethylammonium fixed charge sites surrounded by uncharged polyphenylsulfone, where the polyelectrolyte fiber

content was fixed at 63 wt.% and where the polyelectrolyte ion exchange capacity (IEC) was 2.0 – 2.47 mmol/g, which is below the water solubility limit.

Type B - Polyelectrolyte nanofibers of polysulfone with benzyl trimethylammonium fixed charge sites (2.5-3.1 mmol/g IEC) surrounded by uncharged polyphenylsulfone, where the polyelectrolyte fiber content of the membrane was either 65 wt.% or 55 wt.% and where the polyelectrolyte fibers were partially crosslinked with hexamethylenediamine to prevent dissolution in water.

Type C - Polyelectrolyte nanofibers of polysulfone with either benzyl trimethylammonium, 1-methylimidazolium, or 1,2-dimethylimidazolium fixed charge sites (2.5-3.1 mmol/g IEC) surrounded by uncharged polyphenylsulfone, where the polyelectrolyte fiber content of the membrane was fixed at 65 wt.% and the polyelectrolyte fibers were partially crosslinked with 1,6-hexanediol to prevent dissolution in water.

Type D - Polyelectrolyte nanofibers of poly(phenylene oxide) with benzyl trimethylammonium or 1,2-dimethylimidazolium fixed charge sites (2.5-4.4 mmol/g IEC) surrounded by uncharged polyphenylsulfone, where the polyelectrolyte fiber content of the membranes was either 65 wt.% or 50 wt.% and the polyelectrolyte fibers were partially crosslinked with hexamethylenediamine to prevent water dissolution.

2. All of the nanofiber composite anion exchange membranes were fabricated by simultaneously electrospinning two polymers: uncharged polyphenylsulfone and a polyelectrolyte precursor (either chloromethylated polysulfone, chloromethylated/iodomethylated polysulfone, or brominated poly(phenylene oxide)). Subsequent processing steps after electrospinning converted the dual fiber mats into dense and defect-free membranes, with the following specific steps for each membrane type:

   Type A - Dual fiber mats of chloromethylated polysulfone (CMPSF) and PPSU were immersed in trimethylamine to convert CMPSF into a benzyl trimethylammonium polysulfone polyelectrolyte. Mats were compacted at 5,000 psi for ~20 seconds to increase the fiber volume fraction to ~0.6 and then they were suspended in a tetrahydrofuran vapor atmosphere for 10 minutes at room temperature to allow PPSU to soften, flow and fill the void space between intact polyelectrolyte fibers.

   Types B through D - Dual fiber mats with polyelectrolyte precursor (+ diol crosslinker for type C) and PPSU were electrospun, and the polyelectrolyte precursor was crosslinked by soaking in diamine solution (types B and D) or heating the mat to 110°C for 4 hours (type C). Mats were compacted at 5,000 psi for ~20 seconds to increase the fiber volume fraction to ~0.6, then they were suspended in chloroform vapor for 10 minutes at room temperature to allow PPSU to soften, flow and fill the void space between intact crosslinked precursor fibers. Dense membranes were immersed in a free base solution to convert remaining halomethyl groups after crosslinking to fixed charge sites, where the free bases were either trimethylamine (membrane types B-D), 1,2-dimethylimidazole (type C and D), or 1-methylimidazole (type C only).

3. For membrane types B and C, the chloromethylated or chloromethylated/iodomethylated polysulfone polyelectrolyte precursor was near its maximum degree of halomethylation (97% of possible chloro/iodomethyl sites). Type D membranes employed a brominated poly(phenylene oxide) precursor where the degree of bromination was high (95% of possible bromomethyl sites). In each case, reaction of the precursor polymer with trimethylamine yielded a benzyl trimethylammonium polyelectrolyte that was soluble in water. Thus, crosslinks were necessary to stabilize the AEM.

4. For all membranes, the presence of uncharged polyphenylsulfone limited membrane water swelling and improved the mechanical strength of membranes in the hydrated and dry states. Type A membranes contained 37 wt.% PPSU, where the effective membrane IEC ranged between 1.27-1.56 mmol/g. Type B membranes contained 35 or 45 wt.% PPSU with an effective membrane IEC in the 1.5-2.1 mmol/g range. Type C membranes contained 35 wt.% PPSU and the effective membrane IEC ranged between 1.56 and 2.0 mmol/g. Type D membranes contained 35 or 50 wt.% PPSU and the effective membrane IEC ranged between 1.2 and 2.8 mmol/g.

5. When equilibrated in water at 23°C, nanofiber composite anion exchange membranes where polyelectrolyte fibers were surrounded by uncharged PPSU performed better than homogeneous polyelectrolyte films of the same membrane/effective IEC. For example:

   Type A - A room temperature water-equilibrated nanofiber composite membrane with 63 wt.% polyelectrolyte fibers of 2.47 mmol/g IEC had a higher hydroxide ion conductivity in room temperature water (40 mS/cm vs. 33 mS/cm) and lower gravimetric water swelling (93% vs. 300%) than a homogeneous polyelectrolyte film with 2.47 mmol/g IEC.

   Type C - A room temperature water-equilibrated diol-crosslinked nanofiber composite membrane with 65 wt.% polyelectrolyte fibers of 3.0 mmol/g IEC had higher hydroxide ion conductivity in room temperature water (57 mS/cm vs. 50 mS/cm) and lower gravimetric water swelling (136% vs. 400%) than a homogeneous diol-crosslinked polyelectrolyte film with 2.9 mmol/g IEC.

6. Membranes from types A-D with the best combination of hydroxide ion conductivity, reasonable water swelling, robust mechanical properties, and good chemical stability (for types C and D) are as follows:

   Type A - A composite membrane with 63 wt.% polyelectrolyte (1.56 mmol/g effective membrane IEC) had a hydroxide ion conductivity in water at 23°C of 40 mS/cm, 93% gravimetric water swelling, and 22 MPa stress-at-break when fully hydrated.

   Type B - A composite membrane with 65 wt.% polyelectrolyte and 8% crosslinking degree (2.01 mmol/g effective membrane IEC) had a hydroxide ion conductivity of 65 mS/cm in water at 23°C, a gravimetric swelling in room temperature water of 144%, and a stress-at-break of 13 MPa when fully hydrated.

   Type C - A composite membrane with 65 wt.% polyelectrolyte, benzyl 1,2-dimethylimidazolium fixed charges, and 8% crosslinking degree (1.78 mmol/g effective membrane IEC) had a OH- ion conductivity of 49 mS/cm in water at 23°C, 96% gravimetric liquid water swelling, and 16 MPa stress-at-break when fully hydrated.

Type D - A composite membrane with 50 wt.% polyelectrolyte and benzyl trimethylammonium fixed charges (2.04 mmol/g effective membrane IEC) had a hydroxide ion conductivity of 66 mS/cm in water at 23°C, 97% gravimetric water swelling, and 15 MPa stress-at-break when fully hydrated.

7. The mechanical properties of electrospun and crosslinked composite AEMs were excellent, both in the wet state (with a stress-at-break > 10 MPa) and when dry (where the films were ductile with an elongation at break > 10%. All films could be dried and re-hydrated in the chloride counterion form without physical damage (e.g., cracking).

8. From the fabrication and testing experiments, the following membrane structure/function rules and relationships were found:

   a. The minimum carbon length for effective aliphatic diol or diamine crosslinking of halomethylated polysulfone fibers was 6, i.e., hexamethylenediamine (for membrane types B and D) or 1,6-hexanediol (for type C membranes).

   b. For types B and C membranes where the polyelectrolyte content (65 wt.%) and fixed charge group (benzyl trimethylammonium) were the same, a similar hydroxide ion conductivity and gravimetric swelling in water at 23°C were found when the C6 crosslinker was either a diol or diamine.

   c. For membrane types B and D, ion conductivity was better correlated with the volumetric concentration of fixed charges in the polyelectrolyte (χ, units of mmol charge/cm3 of sorbed water) after water equilibration as opposed to the dry membrane ion exchange capacity (IEC). In these films, the effective membrane value of χ increased with increasing PPSU content and crosslinking (for membranes with 35 wt.% PPSU content only).

   d. For type D films, the best membrane has just enough fiber crosslinks to prevent water solubility of the polyelectrolyte, where PPSU is used to control water swelling, raise the value of χ to promote ion conduction, and improve the mechanical properties of the composite AEM.

   e. Type D membranes with benzyl trimethylammonium fixed charge groups exhibited the best chemical stability in hot alkaline solution. Membrane conductivity showed little or no change over 7 days when immersed in 1.0 M KOH at 60°C.

9. A type D membrane from conclusion 6, with a thickness of 40 μm and an effective IEC of 2.0 mmol/g, was employed in an alkaline H2/O2 fuel cell membrane electrode assembly (MEA) with Pt/C electrodes (0.5 mg/cm2 Pt loading for the anode and cathode). At 60°C, a high peak power density of 320 mW/cm2 was recorded.

4. Publications

A. M. Park and P. N. Pintauro, “Electrospun Composite Membranes for Alkaline Fuel Cells”, *ECS Transactions, Polymer Electrolyte Fuel Cells 11*, **41(1)**, 1817-1826 (2011).

A. M Park and P. N. Pintauro, “Alkaline Fuel Cell Membranes from Electrospun Fiber Mats”, *Electrochemical and Solid-State Letters*, **15**, B27-B30 (2012).

A. M. Park, F. E. Turley, R. Wycisk, and P.N. Pintauro, “Polysulfone-Based Electrospun Anion Exchange Membranes”, *Electrochemical Society Transactions*, **58(1)**, 405-416 (2013).

A.M. Park, F. E. Turley, R. J. Wycisk, and P. N. Pintauro, “Electrospun and Cross-Linked Nanofiber Composite Anion Exchange Membranes”, *Macromolecules*, **47**, 227-235 (2014).

A.M. Park, F. E. Turley, R. J. Wycisk, and P. N. Pintauro, “Diol-Crosslinked Electrospun Composite Anion Exchange Membranes”, *Journal of the Electrochemical Society*, **162**, F560-F566 (2015).

A.M. Park, R. J. Wycisk,X. Ren, F. E. Turley, and P. N. Pintauro, “Crosslinked poly(phenylene oxide)-based nanofiber composite membranes for alkaline fuel cells,” *Journal of Materials Chemistry A*, 2015, DOI: 10.1039/C5TA06209H.

5. Patents

P. N. Pintauro, J. Ballengee, and A. Park, “Composite Membranes, Methods of Making Same, and Applications of Same”, U.S. Patent serial number 13/567,857; publication number US20140349213A1, filed August 2012.